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PRODUCTION OF LOW-MELTING GLAZES WITHOUT FRIT MELTING

A. G. Tkachev,[1] O. N. Tkacheva,[1] and I. S. Solov'eva[1]

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The possibility of using low-melting glazes for decorative ceramics without frit melting is studied. It is demonstrated that a transparent glaze layer can be obtained at a firing temperature not higher than 1000°C provided the initial finely milled material is previously heat-treated at a temperature of 900°C and subsequently milled.

In view of expanding construction, especially that of individual housing, there is a growing demand for decorative elements for room interiors, parks, etc. Ceramic materials offer vast possibilities for making ornamental design elements. The plasticity of the initial material mixture, the variety of tints, the possibility of obtaining virtually any type of surface texture, and the accessibility and relatively low cost of the main components make it possible to produce various articles that are lasting and environmentally safe.

However, the development of this kind of ornamental ceramics has its difficulties. The problem is that such products are needed in limited volumes and yet in a wide product range that frequently changes. Accordingly, such production can be most effectively organized at small companies that are able to promptly respond to changing demands of the customers. At the same time, such small companies have limited possibilities.

This is primarily due to the necessity of using local inexpensive low-melting clays and, consequently, relatively low firing temperatures, whereas the range of low-melting clear glazes offered on the market is limited and the glaze cost is rather high. Recommendations for using raw glazes, i.e., glazes produced directly at factories, are missing from the literature, and the reasons for that are well known.

First, the components that lower the spreading temperature (soda, potash, borax, etc.) are usually electrolytes. Their presence in a glaze slip prevents any control of its flow properties and, accordingly, the deposition of glaze by immersion becomes impossible. Second, the components that pass into the solution impregnate the substrate material when deposited on a molded piece, whereas the insoluble components remain on the surface, i.e., the glaze mixture becomes separated.

We have made an attempt to find an acceptable solution for this problem. The composition for raw opacified glazes for facing tiles proposed in [1, 2] was used as the initial composition: it contained sand, kaolin, pegmatite, calcium borate, zinc oxide, zircon concentrate, and cullet. The casting temperature was 925°C. The advantage of the selected composition is that calcium borate acting as a flux has low solubility in water.

To produce a clear glaze, a series of compositions based on sand, pegmatite, calcium borate, and vitreous ash from a thermal power plant was tested. The slip was prepared traditionally, i.e., the mixture underwent wet milling to a residue of 1.5 – 2.0% on a No. 006 sieve. The glaze slip was deposited on unfired materials by immersion and was fired at 1000°C with a 30 min exposure. The quality of the glaze layer was evaluated visually using a five-grade quality scale. A dull coating with numerous continuity disrupts was graded 0, whereas a lustrous coating without, cracks, shivering, pinpoints, etc. was graded 5. The glaze compositions and their quality estimates are given in Table 1.

It is found that satisfactory spreading of raw glaze at the firing temperature of 1000°C can occur only when the borate calcium content is at least 50%, although to obtain good luster, 60% or higher is needed. Furthermore, in spite of relatively food fusion, all coatings had substantial quantities of gas bubbles that were not removed. Studying the process of the glaze layer formation using high-temperature microscopy demonstrated that the reason for this defect is not so much

TABLE 1

Glaze composition	Weight content, %				Continuity and luster of coating, grade
	sand	pegmatite	TPP ash	calcium borate	
1	30	15	25	30	1
2	20	15	25	40	3
3	10	15	25	50	4
4	–	15	25	60	5

[1] South-Russia State Technical University (NPI), Novocherkassk, Russia.

the elevated viscosity of the glass as the excessively extended period of intense formation and emission of gases from the glaze layer. Consequently, it was concluded that gases need to be removed from raw glaze beforehand, i.e., before applying the glaze to ceramics. For this purpose, the raw glaze slip was dried and heat-treated at successively increasing temperatures; then the heat-treatment product was again milled in wet grinding, deposited on ceramics, and fired at 1000°C; then the coating quality was evaluated.

Degree of fusion of coating depending on the temperature of pretreatment of glaze batch

Treatment temperature, °C	Continuity and luster of coating, grade
650	1
700	1
750	2
800	2
850	4
900	5

As a consequences of the experiments, it was established that preliminary heat treatment at 900°C makes it possible to obtain a lustrous defect-free coating with isolated inclusions of very fine bubbles, which is quite acceptable. The glaze mixture heat-treated at the specified temperature constitutes a highly porous partly fused cake that can be easily crushed. Slip made from this material using the traditional technology has satisfactory parameters of fluidity, sedimentation resistance, and coating ability.

The possibility of converting the flux components of the low-meting compositions, in particular, borax, into the bound water-insoluble state was investigated as well. Mixtures of borax with pegmatite and borax with ash from the Novocherkasskaya thermal power plant were finely milled (2% residue on a No. 006 sieve). The quantity of borax varied from 25 to 50% with an interval of 5%. Milling was performed by the wet method, and the slip was dried and heat-treated at temperatures ranging from 650 to 900°C with a step of 50°C. The heat-treated mixtures were milled until passing through a sieve with a cell size of 1.0 mm, the samples were washed with excess water heated to 80 – 90°C, and the weight losses after washing were determined (Table 2).

Mixtures heat-treated at 900°C were used to prepare slip that was deposited on materials and fired at 1000°C. The evaluation of the resulting coatings is given in Table 3.

Thus, to obtain clear glaze coating of acceptable quality at a firing temperature not greater than 1000°C, it is not necessary to transform the initial material mixture into a homogenous vitreous material, i.e., to melt frit. This operation can be adequately replaced by fine milling of the batch and subsequent heat treatment at 900°C, which is technically feasible even in a small factory. The slip produced by the specified technology can be applied both by immersion and by spraying.

TABLE 2

Borax content, %	Weight loss, % of compositions heat-treated at temperatures, °C				
	650	700	750	800	850
	Weight of borax – pegmatite system				
25	12.9	11.5	6.7	2.8	1.6
30	15.9	15.6	14.8	4.1	1.8
35	17.6	15.2	10.7	5.2	2.8
40	20.1	16.3	10.8	6.6	2.9
45	23.0	17.1	11.6	7.3	3.4
50	25.1	17.8	11.9	7.1	3.8
	Weight of borax – ash system				
25	10.7	7.8	3.4	1.1	0.3
30	12.9	13.3	11.1	2.1	0.2
35	10.1	7.8	6.2	2.3	0.3
40	15.6	11.2	6.7	2.8	0.2
45	16.1	12.8	7.1	3.9	0.3
50	19.8	13.4	8.8	4.6	0.1

TABLE 3

Borax content, %	Continuity of coating, grade, from mixtures of	
	borax – pegmatite	borax – ash
25	1	1
30	1	1
35	2	3
40	2	4
45	4	5
50	4	5

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